Sediment Organic Matter Quality Effects on Pore Water Contaminants

PURPOSE: This technical note examines the effect of sediment organic matter quality on pore water contaminants. Information obtained in the laboratory at the U.S. Army Engineer Waterways Experiment Station, and elsewhere, is included.

BACKGROUND: Over the past 10 years, the U.S. Environmental Protection Agency has pursued development of single-chemical sediment quality criteria (SQC). Equilibrium partitioning of neutral organic chemicals between the organic carbon fraction of bedded sediments and the interstitial water of the sediments provides the theoretical basis for the most popular approach to development of SQC. The solution phase of the chemical in equilibrium with the sediment is considered to represent the bioavailable fraction and to enable the conversion of existing water quality criteria (WQC) into SQC or sediment quality standards.

In this approach, sediment total organic carbon (TOC) is considered to be the primary sediment phase accounting for sorption of neutral organic chemicals, and concentrations of these chemicals are therefore normalized to the TOC fraction. A chemical-unique partition coefficient (K_{OC}), applied to the TOC-normalized chemical concentration, is used to estimate the solution-phase concentration for calculation of the bioavailable fraction, which is then compared with WQC.

One assumption made when deriving SQC from equilibrium partitioning is that all organic carbon will exhibit consistent partitioning behavior. The implicit assumption is that all sediment organic carbon has the same composition, regardless of source.

The U.S. Army Corps of Engineers is presently investigating the link between contaminant levels in sediment and sediment geochemistry, as well as the utility of equilibrium partitioning approaches for predicting toxicity. In the equilibrium partitioning approach, toxicity is assumed to be related to freely dissolved pore water concentrations of contaminants.

The study described in this technical note examined the assumption that all sediment organic carbon behaves similarly.

INTRODUCTION: Concentrations of truly dissolved organic contaminants in sediment pore water are regarded as the contaminant fraction available for organism uptake (Landrum and others 1985; Kukkonen, McCarthy, and Oikari 1990). If all sediment organic carbon does not exhibit comparable partitioning behavior for nonpolar organic contaminants, predicted pore water concentrations will not correspond to actual pore water concentrations.

Evidence suggests that K_{OC} values increase as the aromaticity of sediment organic matter increases (Garbarini and Lion 1986; Chiou and others 1987; Gauthier, Seitz, and Grant 1987; Grathwohl 1990; Murphy, Zachara, and Smith 1990; Zhou, Rowland, and Mantoura 1995).

Nonpolar organic contaminants such as polychlorinated biphenyls (PCBs) and polcyclic aromatic hydrocarbons (PAHs) may also differ in partitioning behavior in the same sediment, depending upon the composition of the organic carbon. Kile and others (1995) reported much higher values of K_{OC} for sediments impacted by anthropogenic contamination than for pristine sediments. Dredged sediments, by virtue of their location, are almost always subject to anthropogenic inputs.

The K_{OC} values for a particular compound have been reported to vary widely between sediments (Schrap and Opperhuizen 1989; Brannon and others 1993, 1995a). Similar wide variations in K_{DOC} for sediment pore waters from different sediments have also been observed (Chin and Gschwend 1992, Brannon and others 1995b). These results imply that partitioning of nonpolar organic contaminants to sediments is much more complex than assumed in the SQC model. Both the form of the contaminant and the organic matter in the sediment have been shown to affect partitioning in ways that are not easily predicted based on sediment organic carbon and contaminant concentrations.

If organic matter quality differs between sediments and the differences affect partitioning, then many of the assumptions used in modeling interactions between nonpolar organic contaminants in sediment and pore waters in aquatic systems are invalid. This study was conducted to examine the impact that changes in sediment organic carbon functionality, including aromaticity, have on pore water concentrations of nonpolar organic contaminants.

ORGANIC CARBON CHARACTERISTICS: Partitioning, or distribution of a hydrophobic organic compound between sediment organic carbon and pore water at equilibrium, is mathematically described as follows:

$$C_W = C_{OC}/K_{OC} \qquad (1)$$

where

C_W = truly dissolved aqueous phase concentration (mg/L)

C_{OC} = concentration of contaminant sorbed to the sediment organic carbon (mg/kg)

K_{OC} = distribution coefficient (L/kg)

This relationship forms the basis for equilibrium partitioning-based SQC (DiToro and others 1991).

Isolation of humic acids from soils and sediments, followed by ^{13}C nuclear magnetic resonance (NMR) (Davis 1993) or Fourier transform infrared (FTIR) analysis (Davis 1993, Brannon and others 1997), indicates that the aromatic character of soils and sediments varies by a factor of 2 or 3 (Table 1). The ^{13}C NMR method provides a measure of the percentage of aromatic functional groups, while the FTIR method coupled with the internal standard facilitates quantitative comparison of peak intensities between different humic sources. Other methods have also been used to estimate the aromatic character of isolated humic acids (Davis 1993, Johnston and others 1994), but the data presented in Table 1 are representative of the spread in aromatic carbon characteristics.

Table 1. Measures of aromatic carbon in soil and sediment organic carbon			
Method	Relative aromatic peak height	% Aromatic functional groups	Reference
^{13}C NMR		23.6 - 47	Davis (1993)
^{13}C NMR		20 - 34	Gauthier, Seitz, and Grant (1987)
FTIR peak height ratios[1]	2.21 - 5.76		Brannon and others (1997)
FTIR peak height ratios[1]	0.39 - 1.13		Davis (1993)

[1] Peak height ratios for humic substance aromatic carbon (1,600 cm^{-1}) functional groups. Peak heights are normalized to the response of the internal standard (potassium thiocyanate, KSCN) at 2,050 cm^{-1} and are in units of mg KSCN/mg humic C.

Results from soil and sediment organic carbon characterizations are mirrored by results of adsorption experiments. Rutherford, Chiou, and Kile (1992) reported that the polarity effect of a sample of soil organic matter on the organic carbon-normalized partitioning of various nonpolar solutes can be measured by determining the partition coefficient of a single nonpolar solute, when compositional analysis of organic carbon is not available. These investigators reported that the calculated variation of organic carbon normalized partitioning was a factor of approximately 3, in agreement with the variability of the results reported in Table 1.

Studies that directly compared ^{13}C NMR and FTIR measures of organic carbon aromaticity to solute partitioning behavior showed that partitioning varied by a factor of 6 (Gauthier, Seitz, and Grant 1987) or a factor of 4 (Brannon and others 1997), for a roughly twofold variation in soil and sediment organic carbon aromaticity. Rutherford, Chiou, and Kile (1992) observed variability of approximately 3, for a roughly twofold change in aromatic carbon. These results indicate that measured values of organic carbon normalized partitioning can result in a three- to sixfold change, for a twofold change in organic carbon aromaticity. Therefore, pore water concentrations of nonpolar organic contaminant would differ markedly for sediments containing the same percentage of organic carbon but varying organic carbon aromaticity.

Results for organic carbon normalized partitioning are generally derived from adsorption studies (Gauthier, Seitz, and Grant 1987; Rutherford, Chiou, and Kile 1992; Davis 1993; Brannon and others 1997). It is becoming increasingly evident, however, that desorption of nonpolar organic contaminants from natural soils and sediments exhibits different behavior from that observed in adsorption studies. Fu, Kan, and Tomson (1994) reported that 30 to 50 percent of PAHs adsorbed by sediment resisted desorption. Desorption rates of PAHs were from 1 to 3 orders of magnitude smaller than previously predicted or measured by adsorption/desorption studies and could not be explained by kinetic models or artifacts of the procedure (Kan, Fu, and Tomson 1994).

The maximum concentrations resistant to desorption for one sediment were found to be 10 mg/kg for naphthalene and 0.36 mg/kg for PCB 52 (Kan and others 1997). These values can be expected

to vary from sediment to sediment, but are illustrative of the potential impact of the resistant fraction on desorption. The irreversibly adsorbed contaminant is apparently in an energetically more stable environment than that normally associated with adsorption of nonpolar organic contaminants (Kan and others 1997). This phenomenon will be present in sediments subject to anthropogenic inputs and will result in pore water contaminant concentrations lower than predicted by equilibrium partitioning theory even if the effect of organic carbon quality is not considered.

OTHER ORGANIC CARBON SOURCES: Dredged sediments are located in shipping channels and harbors and can be expected to contain organic carbon sources different from those in more pristine environments. Brannon and others (1991) reported finding coal in Red Hook sediment from the New York Bight. It is highly probable that this is not an isolated occurrence. Coal fines can be transported to receiving waters by storm events in high quantities, producing a coal-contaminated sediment system (Shorten, Elzerman, and Mills 1990). Coal contains substantial amounts of PAHs (Shorten, Elzerman, and Mills 1990), which may be measured in total sediment analyses but will exhibit markedly lower desorption than sediment-bound PAHs.

Equilibrium partitioning relationships developed for PAHs and sediment organic carbon are based on adsorption studies in which all the contaminant added was available for partitioning (DiToro and others 1991). However, Burford, Hawthorne, and Miller (1993) found that none of the spiking procedures they investigated was able to accurately represent the native analytes, which were normally bound much more strongly by the environmental matrices than were the spiked analytes.

Puschel and Calmano (1995) reported that, even for sorption, individual PAH compounds behaved differently, displaying behavior that could not be explained by organic carbon normalization or by the use of a reference compound. With time, contaminants added to soils become increasingly more resistant to biodegradation and extraction (Hatzinger and Alexander 1995). The fraction of contaminant in soils and sediments that is resistant to desorption can constitute half or more of the total contaminant concentration (Pavlostathis and Jaglal 1991, Carroll and others 1994).

A growing body of evidence shows that a large fraction of the total PAH concentration in sediments is unavailable for partitioning into pore water due to PAH inclusion in combustion-derived particles (McGroddy and Farrington 1995; McGroddy, Farrington, and Gschwend 1995; Maruya, Risebrough, and Horne 1996). In a field study in San Francisco Bay, Maruya, Risebrough, and Horne (1996) reported that the presence of soot and combustion-derived PAHs, together with substrate heterogeneity, invalidated or at best limited the utility of simple equilibrium models used to develop quantitative SQC for accurate prediction of bioavailable PAH concentrations. McGroddy and Farrington (1995) reported that only 0.2 to 5 percent of sediment phenanthrene concentrations appeared to be readily available to partition into pore water. Sediment pyrene was more variable, but the amount available for partitioning into pore water ranged from 5 to 70 percent (McGroddy and Farrington 1995). These results indicate that pore water concentrations of these PAH compounds predicted by equilibrium partitioning would be greatly overestimated because sediment analysis includes forms of the contaminant that are unavailable for partitioning.

Development of a method for quantification of soot carbon (SC) in sediment has facilitated evaluation of SC impacts on PAH partitioning. Gustafsson and others (1997) found that in a freshwater lake sediment, SC constituted between 1.8 and 6.4 percent of sediment organic carbon,

while SC constituted approximately 12 percent of sediment organic carbon from Boston Harbor sediment. Addition of a SC term to the partition model quantitatively explained the elevated PAH K_D values (a result of lower pore water PAH concentrations) of two marine sediment-pore water systems (Gustafsson and others 1997). The authors were of the opinion that the influence of PAH-soot associations was so large that the effects of such associations on the bioavailable fraction should be taken into account in the establishment of SQC. Gustafsson and others (1997) proposed the equation

$$K_D = f_{OC}K_{OC} + f_{SC}K_{SC} \qquad (2)$$

where

$\quad$ K_D $\quad$ = partition coefficient (L/kg$_{sediment}$)

$\quad$ f_{OC} $\quad$ = weight fraction of organic carbon in the sediment

$\quad$ f_{SC} $\quad$ = weight fraction of soot carbon in the sediment

$\quad$ K_{SC} $\quad$ = chemicals soot-carbon-normalized partition coefficient

Application of this equation to pore waters from Boston Harbor sediment has shown close agreement with measured in situ partitioning coefficients (Gustafsson and others 1997). These results clearly demonstrate the importance of SC in controlling partitioning of PAHs to pore waters and the impact that such partitioning will exert on SQC. Incorporation of the $f_{SC}K_{SC}$ term into SQC would result in greatly increased values of PAH SQC because of the impact that sediment SC has on lowering the partitioning of PAHs to pore water.

PAHs that do not partition into pore water are not available for uptake by organisms. This limitation on PAH bioavailability was demonstrated by McFarland and Ferguson (1994), who found that the biota/sediment accumulation factors (BSAFs) of PAH compounds in shellfish exposed to contaminated sediments were about 20-fold lower than the BSAFs reported for chlorinated compounds. These findings demonstrate that organic carbon normalization used to calculate SQC cannot accurately predict pore water PAH concentrations in sediments containing combustion-derived PAHs. Use of SQC in such sediments will greatly overestimate the impacts of sediment PAHs on biota.

CONCLUSIONS: The quality of organic carbon as reflected by aromaticity varies by a factor of 2 to 3. For a twofold change in soil and sediment aromaticity, partitioning behavior of nonpolar organic contaminants varies by a factor of 4 to 6. Therefore, pore water concentrations of nonpolar organic contaminants would differ markedly for sediments containing the same percentage of TOC but varying by a factor of 2 in organic carbon aromaticity.

Sediments also contain other organic phases, such as coal and soot, that markedly lower partitioning of PAHs into pore water (Table 2). The influence of PAH-soot associations on pore water partitioning is so pronounced that alternate equations incorporating the effects of soot on PAH partitioning have been proposed for SQC. Equilibrium partitioning models based on the assumption

Table 2. Factors affecting prediction of sediment pore water nonpolar organic contaminant concentrations predicted by equilibrium partitioning	
Factor	**Reference**
Organic carbon aromaticity	Gauthier, Seitz, and Grant 1987; Davis 1993; Brannon and others 1997
Irreversible adsorption	Kan, Fu, and Tomson 1994; Fu, Kan, and Tomson 1994; Kan and others 1997
Coal	Shorten, Elzerman, and Mills 1990; Brannon and others 1991
Combustion-derived PAHs	McGroddy and Farrington 1995; McGroddy, Farrington, and Gschwend 1995; Maruya, Risebrough, and Horne 1996; Gustafsson and others 1997

that the sorption behavior of all sediment organic carbon is equivalent predict erroneous pore water concentrations of nonpolar organic contaminants.

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